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High-throughput viscosity determinations

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A new high-throughput viscosimeter device was designed, built, and tested allowing measurement of the viscosity of 100 different solutions in a single experiment using the falling sphere approach. Using the corrected Stokes’ law, viscosities obtained by the HT device were compared to viscosities of the same solutions obtained on a conventional viscosimeter and showed excellent correlation. The theoretical set of data, correlated with Reynolds numbers, and the viscosities obtained for each sample showed very good correlation with the experimental data, demonstrating the robustness of the device. © 2008 American Institute of Physics. [DOI: 10.1063/1.2976350]

I. INTRODUCTION

High-throughput and robotic methodologies have enabled the routine preparation and generation of large numbers of formulations in a highly efficient manner.1-3 This ability, however, then brings to the fore the requirement to rapidly characterize the formulations that are generated, with the need to determine a range of physical parameters, which includes viscosity and density.4 Viscosity is an especially important feature of fluids, relating to their resistance to deformation5-7 and plays an important role in not only understanding their behavior but also dictating the possible applications any specific fluid. Experimental viscosity measurements are thus very important in many industrial areas, for example, in printing or spraying processes, which require materials that fall within specific viscosity regimes in order to have practical application; and thus with high-throughput formulation generation a need arises to be able to determine the viscosity of large numbers of samples in a parallel way.

Flow regimes are classified into laminar, transitional, and turbulent flow, with the specific flow conditions distinguished by so-called Reynolds numbers (Re) a dimensionless unit proportional to [(inertial force)/(viscous force)]. When Reynolds number is small, the fluid’s viscosity is dominant and, in this situation, fluid is described as being in laminar flow (and Stokes law applies). When the Reynolds number is large the fluid’s inertial effects rule and turbulent flow dominates (the flow conditions between laminar flow and turbulent flow are known as transitional flow).

There are four main types of viscometers designed to measure liquid viscosity:4-10 capillary viscometers, rotational viscosimeters, falling sphere, and vibrational viscosimeters, but the falling sphere approach has attracted attention due to simplicity of operation (the falling sphere approach allows fluid viscosity to be determined using gravitational effects and is described by Stokes’ law):"
was based on rolling of the ball inside the capillary at different inclinations (from 20° to 70°). In these experiments the measurement of the viscosity was calculated taking the capillary through an inclination angle of 50° to get data comparable to the HT viscometer.

D. Characterization of density and standard viscosity

The density of each sample solution was measured by a liquid density transmitter L-DENS. The standard viscosity of each sample solution was measured using an automated microviscometer useful for a viscosity range from 80 to 2500 mPa s and was based on the falling ball principle. This consisted of a glass capillary (4 mm diameter × 15.8 cm length with a stainless steel ball (3 mm diameter and a density of 8.75 g/ml). The measurement of dynamic viscosity was based on rolling of the ball inside the capillary at different inclination angles (from 20° to 70°). In these experiments the measurement of the viscosity was calculated taking the capillary through an inclination angle of 50° to get data comparable to the HT viscometer.

III. RESULTS AND DISCUSSION

A. Experimental, wall, and end corrections

As mentioned above Stokes’ law has limitations as it is valid only for laminar flow. In reality, the true terminal velocity of the falling ball must be corrected with respect to the determined experimental velocity value. This correction for terminal velocity is due to the fact that Stokes’ law works well only in fluid media with no inertial forces (when the ball moves slowly with no acceleration), no end effects (the ball falls steadily) and no wall effect (infinite Newtonian media). In practical experiment, wall, inertial, and end effects need to be corrected for and K factors must be calculated to compensate for deviations in Stokes’ law caused by experimental procedures. In this case corrections for wall and end effects were carried out, but no corrections were necessary for the inertial effect due to the slow motion of the ball inside the measurement tube.

A reference experiment was first performed using a single tube and pure glycerol. The time needed (t= 790 s) for a PVC sphere to reach the bottom of a single tube (10.4 cm long) in pure glycerol was measured and used in the corrected Stokes’ Eq. (2) to calculate the experimental correction factor $K_0 = 0.0787$.

$$K = 18 \mu V/d^2g(p_1 - p_2) = 18 \mu V/(d^2g(p_1 - p_2)t).$$

The second correction considered the wall effect, being the ratio between experimental and corrected terminal velocities calculated considering the ratio $d/D$, using three equations:

(a) Francis equation,

$$V/Vc = K_1 = [(1 - (d/D))/1 - 0.475(d/D)]^3.$$  

(b) Ladenburg equation,

$$V/Vc = K_2 = 1/[1 + 2.1(d/D)].$$

(c) Faxen equation,

$$V/Vc = K_3 = (1 - 2.104(d/D)^3 + 2.09(d/D)^5 - 0.95(d/D)^5).$$

The values of the K factors considering the wall effect correction are as follows: $K_1 = 0.098$, $K_2 = 0.442$, and $K_3 = 0.115$.

The third correction considered the end effect. This was calculated considering various distances (h) of the ball with respect to the bottom of the tube, to ascertain the constant velocity nature of the ball falling into the tube. Values of h close to zero were studied: 0.0002, 0.00025, 0.0003, and 0.0004 m (the tube was 0.104 m). The equation for the end effect is as follows:

$$V/Vc = [1 + (9/8)d/(2h)]^{-1} = K.$$  

Four values of K were determined as a function of h:

$K_4 = 0.0689$ (h=0.0002); $K_5 = 0.0847$ (h=0.00025); $K_6 = 0.1$ (h=0.0003); $K_7 = 0.129$ (h=0.0004).

B. High-throughput measurement of viscosities

The traveling time of a PVC sphere going through the sample solution was recorded by a web camera with each “hole” representing a sample solution. From Fig. 2 it can be seen, at the beginning, that all the holes were empty (the holes were bright). 100 s later, some holes were filled with spheres and became dark, and the number of dark holes increased with time. At 808 s all the holes were filled with spheres and became dark as shown in Fig. 2. Using this approach the time of the fall in each well was obtained and based on the corrected Stokes’ law equation as follows:
In order to study the performance of the high-throughput viscosity measurement device the viscosity of 100 samples were determined using both the HT device and a conventional automated viscosimeter. Corrections of terminal velocity $V_C$ (considering experimental, wall, and end effects) were

\[ \mu = K_o d^2 g (\rho_1 - \rho_2) / (18 V_C). \]  

(7)

In order to study the performance of the high-throughput viscosity measurement device the viscosity of 100 samples were determined using both the HT device and a conventional automated viscosimeter. Corrections of terminal velocity $V_C$ (considering experimental, wall, and end effects) were

<table>
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FIG. 2. Sphere shadow pictures. (a) $t=0$ s, (b) $t=100$ s, (c) $t=300$ s, (d) $t=650$ s position, (e) $t=750$ s, and (f) $t=808$ s.
calculated for the HT values and correlations between these data and conventional viscosity data were carried out, as shown in Fig. 3.

Figure 3 shows the correlation between conventional viscosity data and the data obtained with the HT viscometer device (with experimental, end, and wall corrections). It can be said that most of the lines were very close each other and showed excellent correlation with the conventional viscosity data. As expected the wall effect correction constant from Francis’ equation \(K_1\) worked very well as in this case \(d/D\) is equal to 0.6 which is within the range of Francis’ equation \(d/D < 0.9\) \(K_1 = 0.098\) very close to the experimental correction factor \(K_0 = 0.079\). On the other hand the viscosity data using Ladenburg’s constant \(K_2\) showed the biggest discrepancy as the \(d/D\) values should be lower than 0.1 for this equation to apply.

Experimental final velocities were calculated using the correction factors \((K_0, K_7)\) and using the following equations:

\[ V_{\text{exp}} = L/t, \]  

\[ V_c = V \exp/K_n. \]  

(9)

Reynolds numbers were taken in the range from 0.01 to 1.55 and were introduced into the Eqs. (10) and (11) to determine theoretical viscosity and theoretical terminal velocity.

\[ \mu = [(4r^3g(p_1 - p_2)(\rho_1 - \rho_2))/(9 \, Re)]^{1/2}, \]  

(10)

\[ V = (Re \, \mu)/(d \rho_2). \]  

(11)

The corrected experimental velocities (with different \(K_n\) values) were compared to the theoretical terminal velocities as shown in the Fig. 4.

Figure 4 shows that the terminal velocities of the samples determined with the HT viscometer increased as the time of the fall of the ball increases. It can be seen that long fall times (100–1000 s) at all the terminal velocities were very close, suggesting high sample viscosity and low Reynolds number and low deviation from Stokes’ law. Theoretical velocity values estimated with low values of Reynolds numbers were very close to the corrected terminal velocities corresponding to the wall effect corrections \((K_1)\), end effect \((K_6)\) and the experimental correction factor \((K_0)\).

Reynolds numbers for the HT viscometer were also calculated using

\[ \text{Re} = 2 \rho_2 r V/\mu = 4r^3 \rho_2 (p_1 - p_2) g/9 \mu^2. \]  

(12)

Figure 5 shows that there is a dramatic deviation of the Reynolds numbers of the samples from both devices; however, the viscosity values are very similar in both cases due to the corresponding correction constants. It can be said that for low Reynolds number values in the range from 0.1 to 0.01, the majority of the samples in both devices coincides, because the viscosity values in both of them are higher and thus Stokes’ law complies very well. On the other hand there are deviations in both devices when the Reynolds numbers are in the range from 0.1 to 0.5, due to the low viscosity of the samples as well as the physical parameters of each device such as spheres (size and density), the lengths and diameters of the capillary (conventional viscometer) and tubes (HT).
C. Statistical treatment

Statistical analysis based on both descriptive analysis and viscosity values comparisons were carried out. Descriptive analysis allowed determination of the main statistical descriptors for each viscosity data set determined for each correction factor ($K_0$ and $K_5$) and for the standard viscometer. Test analyses were carried out by analysis of the correction factors determined from the high-throughput viscometer and those determined using the standard viscometer. Despite the many correction factors determined, those with the best fit with the viscosity values of the standard viscometer were chosen, with two correction factors $K_0$ (experimental) and $K_5$ (end effect for $z=0.00025$) selected.

1. Descriptive analysis

This was carried out by considering an analysis of the distribution of each population of viscosity values, determined individually, for each correction factor with the standard viscometer. This analysis was based on the study of cumulative frequency, which gives the values of the viscosity population for a given value of percentage, considering 100% of the population. Analysis of the data distribution was carried out as shown in the Table II.

Table II shows that the data distribution was not symmetric with a skew to the right. It was found that when comparing, both the mean and the standard error of the standard viscometer with the HT viscometer ($K_0$), their values were nearly identical, however, there was more variation in the case of the standard viscometer when compared to the HT viscometer, with a $K_5$ value of 6.32% for the mean and 8.85% for the standard error.

For lower values of the percentile (10% to 25%), the data distribution showed viscosity values were virtually identical for the standard and the HT viscometer ($K_0$). The data distributions were indeed similar for the case of the standard viscometer and the HT viscometer ($K_5$), for percentile values equal or greater than the median values.

Confidence intervals from the HT and the standard viscometers were determined as shown in Table III.

2. Viscosity value comparison: Test analysis

The comparison was carried out comparing the results of the standard viscometer (reference) and the HT viscometer, using two factor corrections: $K_0$ (experimental) and $K_5$ (end effect for $z=0.00025$) as follows.

Partial least square analysis. In this case correlation analysis was carried out to check the fit of both correction factors with the standards, with analysis carried out using linear regression, using

$$y = a + bx.$$  (12')

The partial least-squares analysis gave the main parameters as shown in Table IV.

Table IV shows that there was good correlation between the two correction factors (slope $b$ were very similar, with only approximately 7% of variation), while their intercepts ($a$), had only 5.7% variation. However the standard error of the estimate ($S_{yx}$) of the regression was higher in the case of the comparison with the correction factor ($K_5$) than the comparison of the correction factor ($K_0$) (approximately 8.6% of variation).

**Fisher distribution-test.** A Fisher distribution-test ($F$-test) was used with the aim at comparing the variance of two populations using a one-tailed test for $p=0.05$. This comparison was carried out by determining the $F$ ratio of the two populations as shown in expression (13) and comparing the ratio with a critical value of the Fisher distribution ($F_{cr}$ = 1.394) for a distribution with 95% and 99% degrees of freedom.

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<tr>
<th>Data distribution (%)</th>
<th>HT viscometer (correction factor: $K_0$) (mPa s)</th>
<th>HT viscometer (correction factor: $K_5$) (mPa s)</th>
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<td>489 ± 55</td>
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<td>485 ± 73</td>
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**TABLE IV. Main parameters of the PLS analysis.**

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<th>$b$</th>
<th>$r^2$</th>
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freedom (ν).

If the variance of the population 1 [σ²(1)] is similar to the population 2 [σ²(2)] and F < Fc, then the two populations have the same variance.

\[ F = \frac{\sigma^2(1)}{\nu_2/\sigma^2(2)} * \nu_1. \]  

(13)

In this case, comparison of the viscosity data set for the two factor corrections (K₀ and K₃) with the viscosity values of the standard viscometer was carried out looking at the F ratio of variance, considering a 5% confidence level (p=0.05), and a one tail distribution.

Table V shows the values of F determined for the viscosity values of the HT method for each correction factor and the viscosity values for the standard viscometer.

Table V shows that F < Fc for both correction factors. Furthermore their p values were greater than p=0.05, and so the viscosity values determined by the HT method, for both correction factors (K₀ and K₃) were not significantly different compared to those determined by the standard viscometer.

Moreover it can be said that the viscosity values of the two correction factors (K₀ and K₃) were precise, with viscosity value of K₀ being more precise than those belong to K₃.

z Test. This test shows whether the sample mean and the population mean between the two populations is statistically significant. Therefore for z > zc, the values of the comparison of the sample mean (chosen randomly) with the population mean were significant at p=0.05. Therefore the comparison of the HT viscosity values of the correction factors (K₀ and K₃) and the standard viscosity values was carried out considering expression (14), for a zc = 1.645 and for p = 0.05.

\[ z = \frac{(X_{HT} - X_s)}{(\mu_{HT} - \mu_s)}/(\sigma^2_{HT}/N_{HT} + \sigma^2_s/N_s^{1/2}). \]  

(14)

In this z test, ten samples were chosen randomly from each population of the viscosity for each correction factor (K₀ and K₃) and the sample mean difference between each correction factor of the HT (XₜHT) with the Standard (Xₛ) analyzed to see if it complied with the expressions of the null hypothesis (H₀) (15) or the alternative hypothesis (H₁) (16).

\[ H₀: (X_{HT} - X_s) \leq 150 \quad \text{(sample mean difference no significant at } p = 0.05), \]  

(15)

\[ H₁: (X_{HT} - X_s) > 150 \quad \text{(sample mean difference significant at } p = 0.05). \]  

(16)

The values of these sample mean differences (XₜHT - Xₛ) were higher than the values of the difference of the population mean (μₜHT - μₛ), being −3.5 mPa s for the case of the correction factor (K₀) and 33.7 mPa s for the case of the correction factor (K₃), respectively. For each correction factor (K₀ and K₃) of the HT viscometer and its comparison with the standard viscometer the following results (Table VI) were generated.

Table VI shows that the higher the sample mean difference between the correction factors of the HT and the standard viscometers the higher the z values were and so the differences between the sample means were significant. Therefore it can be said that for sample mean difference ±150 mPa s, the difference between the viscosity values of the correction factors and the standard viscometer was not significant and z < zc, complying with the null hypothesis.

On the other hand for the correction factors with viscosity values of 250 mPa s more than the viscosity values of the standard viscometer, the difference was significant because the probability (p values) was very low and <0.05.

IV. CONCLUSIONS

A high-throughput viscosity measurement device was fabricated based on the principle of a falling sphere viscometer and assisted sphere shadow methodology. A series of 100 glycerol/water fluids was used to test and validate the high-throughput viscosity measurement device in comparison to a traditional viscometer. The results demonstrated that the high-throughput viscosity measurement device worked exceptionally well under low Reynolds number flow conditions, and that this device could be considered as an easy to use and low cost novel measurement device. The one limitation was that because light must pass through the fluids, the device is limited to physically similar transparent solutions.

Statistical treatment showed a slightly skewed trend, but the data distribution was similar to the standard viscometer with similar standard errors. Partial least-squares (PLS) analysis gave good correlation coefficients, while F and z tests showed precision and accuracy in the comparison of the correction factors (K₀ and K₃) from the HT and standard viscometers.

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**TABLE VI. z -test values for the method and reference comparison.**

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<tr>
<th></th>
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<tr>
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<td>0.305</td>
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<td>0.022</td>
<td>1.66</td>
<td>0.048</td>
</tr>
</tbody>
</table>
V. Supplemental material available

Supplemental tables with the determination of density, viscosity, Reynolds numbers of the 100 samples, and the velocity of the ball inside the device, for both the HT and the standard viscometer devices are available, as well as the data for the theoretical values of Reynolds number, viscosity, and velocity.

ACKNOWLEDGMENTS

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NOMENCLATURE

\( \mu_s \) = viscosity mean value of the population of the Standard viscometer
\( \rho_1 \) = ball density (kg/m)
\( \rho_2 \) = sample density (kg/m)
\( g \) = gravity acceleration (9.8 m/s^2)
\( V_{exp} \) = experimental velocity (m/s)
\( V_{c} \) = corrected velocity (m/s)
\( V \) = theoretical velocity (m/s)
\( \rho_1 \) = ball density (kg/m)
\( \rho_2 \) = sample density (kg/m)
\( \mu \) = viscosity (mPa s)
\( \rho_{1} \) = ball density (kg/m)
\( \rho_{2} \) = sample density (kg/m)
\( g \) = gravity acceleration (9.8 m/s^2)
\( V_{exp} \) = experimental velocity (m/s)
\( V_{c} \) = corrected velocity (m/s)
\( V \) = theoretical velocity (m/s)
\( \mu \) = viscosity (mPa s)
\( \rho \) = density
\( a \) = intercept
\( b \) = slope
\( r^2 \) = correlation coefficient
\( S_{St} \) = standard error of estimate
\( X_{HT} \) = viscosity mean value of the chosen ten samples from the HT viscometer
\( X_{S} \) = viscosity mean values of the chosen ten samples from the standard viscometer
\( \mu_{HT} \) = viscosity mean value of the population of the HT viscometer

\( \mu_s \) = viscosity mean value of the population of the Standard viscometer
\( \rho_1 \) = level of significance
\( V_{1} \) = freedom degree of population 1
\( V_{2} \) = freedom degree of population 2
\( \sigma_{HT}^2 \) = variance of the viscosity values of the HT viscometer
\( \sigma_{S}^2 \) = variance of the viscosity values of the standard viscometer
\( N_{HT} \) = number of observations of the population belong to the HT viscometer
\( N_{S} \) = number of observations of the population belong to the standard viscometer